# The growth of $GaF_3$ films on GaAs(110) at elevated temperatures studied with soft x-ray photoelectron spectroscopy

W. C. Simpson, T. D. Durbin,[a] P. R. Varekamp, and J. A. Yarmoff[b]
*Department of Physics, University of California, Riverside, California 92521 and Materials Sciences Division, Lawrence Berkeley Laboratory, Berkeley, California 94720*

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The growth of $GaF_3$ films on GaAs(110) wafers via exposure to $XeF_2$ is studied as a function of substrate temperature with soft x-ray photoelectron spectroscopy. For temperatures between 300 and 550 K, a $GaF_3$ film forms with an interface to the substrate consisting of GaF, elemental As and possibly some AsF. In this temperature range, the films thicken with exposure up to a limit of ~15 Å. The initial F uptake rate increases with elevated substrate temperature without altering the limiting thickness. In addition, there is little variation in the thickness or composition of the film–substrate interface over this temperature range. Above 550 K, $XeF_2$ etches GaAs, leaving a GaAs surface covered with ~1 monolayer of elemental As. A film growth mechanism is discussed to explain these results. © *1995 American Institute of Physics.*

## I. INTRODUCTION

Microelectronic devices manufactured from GaAs are becoming more prevalent, but progress in the development of GaAs-based devices has been hindered by the lack of high quality insulator–GaAs interfaces. A potential candidate material to be used as an insulator is $GaF_3$, and much work is being done to characterize the $GaF_3$–GaAs system. A simple chemical process for growing $GaF_3$ films is to expose GaAs to a gaseous F-containing compound, in a manner similar to $SiO_2$ growth on Si via exposure to $O_2$. This has been demonstrated in the reactions of GaAs with $CF_4$,[1–5] $CHF_3$,[6] and $CCl_2F_2$ plasmas,[7–10] $XeF_2$ vapor,[11,12] $F_2$ gas,[13–15] atomic F,[16] and $F^+$ ions,[6] which, in all cases, produce $GaF_3$ films. To be technologically useful, the $GaF_3$–GaAs interface should be atomically abrupt, with a low density of interface states. Operational devices have been constructed from $GaF_3$–GaAs structures, demonstrating that the interface state density can be reduced to a sufficiently low level.[14] The challenge, then, is to find the appropriate conditions for growing an atomically abrupt $GaF_3$–GaAs interface via exposure to F.

A good first step for determining these conditions is to develop an understanding of the fundamental chemistry involved in the reaction of atomic F with GaAs. High-resolution soft x-ray photoelectron spectroscopy (SXPS) is well suited for studying this reaction. Since SXPS utilizes tunable synchrotron radiation, photon energies can be selected so that only the outermost atomic layers are probed. This is essential for monitoring the initial reaction at the surface, as well as for following subsequent subsurface reactions. Also, SXPS is a core-level spectroscopy and, as such, can be used to determine both the concentrations and the local chemical environments of the individual species present in these first few layers of the surface.

Two previous studies have utilized high-resolution SXPS to investigate the room-temperature reaction of atomic F with GaAs, using $XeF_2$ vapor as the source of atomic F.[11,12] $XeF_2$ was chosen because of its ease of handling and because it readily dissociates on a GaAs surface, liberating atomic F. McLean *et al.*[11] used SXPS to investigate the room-temperature reaction of atomic F with cleaved GaAs(110) surfaces. It was found that the reaction forms $GaF_3$, as well as some intermediate products, and that As is removed from the near-surface region as a result of the reaction. Varekamp *et al.*[12] employed electron energy loss spectroscopy (EELS), photon-stimulated desorption (PSD), and SXPS to study the electronic structure of $GaF_3$ films grown at room temperature on both GaAs(110) and (100) wafers. It was shown that the F/GaAs reaction product distribution is independent of the crystal face and initial surface order, and that films as thin as 10 Å develop the electronic band structure of bulk $GaF_3$. In addition, it was shown that the film growth is spatially homogeneous, but that annealing leads to the inhomogeneous desorption of $GaF_3$.

To date, there have been no high-resolution SXPS studies of the effects of temperature or pressure on the reaction of atomic F with GaAs. The present work uses SXPS to investigate how the substrate temperature ($T_s$) during film growth affects the $GaF_3$–GaAs interface for films grown on GaAs(110) wafers via $XeF_2$ exposure. As no significant differences in the growth of $GaF_3$ via $XeF_2$ are observed between the (100) and (110) crystal faces, the results found here are expected to extend to the (100) surface as well.[12] It is found that increasing the substrate temperature from 300 to 550 K causes no appreciable differences in the chemical composition of the interface, but only a slight thickening of the $GaF_3$ film. There is a limit to the thickness of films that can be grown with low pressures of $XeF_2$ vapor, however, which was overcome by substantially increasing the pressure. For reactions at temperatures above 550 K, $XeF_2$ etches GaAs, producing a GaAs surface covered with ~1 monolayer of elemental As.

## II. EXPERIMENTAL PROCEDURE

Two *p*-type GaAs wafers, cut to within ±0.5° of the (110) plane and doped with Zn to a concentration of $10^{18}$

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[a] Present address: College of Engineering, Center for Environmental Research and Technology, University of California, Riverside, CA 92521.
[b] E-mail:yarmoff@ucr.edu

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cm$^{-3}$, were used in this experiment. Both were etched in a 1:1:200 solution of $HNO_3$:$H_2O_2$:$H_2O$, rinsed with deionized water and dried with isopropanol before being placed in the ultrahigh vacuum (UHV) chamber. The samples were cleaned in UHV by sputtering with 500 eV $Ar^+$ ions, followed by annealing to $\sim$825 K. This cleaning procedure generates a slightly Ga-rich surface due to selective sputtering of As.[17,18] It was not possible to directly measure the sample temperature during $XeF_2$ exposure or annealing. Instead, a calibration of current to temperature was made for each sample, prior to its use, with an infrared pyrometer. Then, to heat the sample, the appropriate current was run through the Ta foil on which the sample was mounted. Thus, reported temperatures have an estimated uncertainty of $\pm$25 K.

Samples were exposed to $XeF_2$ in a separate stainless steel UHV chamber, which had a typical base pressure of $\sim 5 \times 10^{-10}$ Torr. Sample transfers between the dosing chamber and the analysis chamber were carried out entirely under UHV. The dosing chamber was passivated with a large amount of $XeF_2$ prior to any exposures to reduce vapor phase transport of metal fluorides to the sample surface.[19] A cold cathode ion gauge was used to monitor the pressure in the dosing chamber in order to avoid the creation of both metal fluorides and radical species from the hot filament of a conventional ion gauge. No evidence of metal contamination was apparent in any of the SXPS spectra collected. Two $XeF_2$ exposures, 10 and 100 kL (1 kL$=10^3$ L; 1 L$=10^{-6}$ Torr$\cdot$s) were used in the first part of this experiment. The 10 kL exposure was for 1000 s at a pressure of $10^{-5}$ Torr, and the 100 kL exposure was for 1000 s at a pressure of $10^{-4}$ Torr. In the second part of the experiment, several exposures were carried out at a single $T_s$ of 550 K, all at pressures less than $3 \times 10^{-6}$ Torr. Finally, a thick $GaF_3$ film was grown by exposing GaAs to $\sim$4 Torr of $XeF_2$ for 1000 s at room temperature, which is a $4 \times 10^6$ kL exposure. In all cases, the sample was heated to the appropriate temperature, $T_s$, prior to exposure and the $XeF_2$ vapor was pumped out before the sample was cooled to room temperature for measurement.

The experiments were performed at the National Synchrotron Light Source, Brookhaven National Laboratory, on beamline UV-8a. The SXPS spectra were collected with an angle-integrating ellipsoidal mirror analyzer, which accepts photoelectrons emitted from the sample within an $\sim 85^\circ$ cone centered about the surface normal.[20] The photon energy was selected with a 3 m focal length grazing incidence toroidal grating monochromator. The high-resolution SXPS spectra have a combined energy resolution of $\sim$0.15 eV. All SXPS spectra were collected at room temperature. Variations in the incident photon flux were monitored by the total photocurrent at the final focusing mirror and, in all spectra, the $y$ axis represents the measured photoelectron intensity divided by the incident photon flux. After each exposure, care was taken to consistently reposition the sample in the analyzer so that spectra from different exposures could be compared to each other.

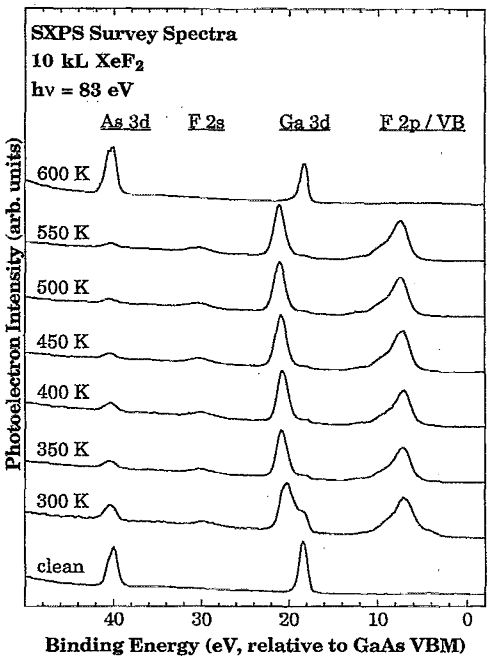

FIG. 1. SXPS survey spectra collected from GaAs(110) surfaces exposed to 10 kL of $XeF_2$. Spectra are scaled to the same maximum peak height, and are labeled with the temperature of the substrate during exposure.

## III. RESULTS

SXPS survey spectra, containing the valence band and the Ga $3d$, As $3d$, and F $2s$ core levels, are shown in Fig. 1 in order of increasing $T_s$ for samples exposed to 10 kL of $XeF_2$. Binding energies are given with respect to the GaAs valence band maximum (VBM), which removes band bending effects. Upon fluorination, there is a noticeable increase in valence band intensity at $\sim$6 eV due to a contribution from F $2p$. This feature, present in the spectra for dosing temperatures up to 550 K, grows rapidly with exposure and is a very sensitive measure of the presence of F on the surface.[12] Fluorination also causes a broadening toward higher binding energy (BE) of the Ga $3d$ and As $3d$ core levels, as well as the formation of a strong chemically shifted Ga $3d$ component. There is a very little difference in the qualitative behavior of the survey spectra for temperatures below 600 K. However, for $T_s$=600 K, the F $2p$ feature in the valence band, as well as the F $2s$ level and the shifted Ga $3d$ component, are absent from the survey spectrum.

Background-subtracted high-resolution Ga $3d$ and As $3d$ core-level spectra, plotted with respect to the substrate $3d_{5/2}$ component, are shown in Figs. 2 and 3, together with numerical fits to the data. High-resolution $3d$ core-level spectra were collected from all of the fluorinated surfaces, but only four representative spectra are shown. The photon energies used to collect these spectra were selected so that the measured photoelectrons all have kinetic energies of $\sim$35 eV, thereby maximizing the surface sensitivity of the measurement by minimizing the escape depth of the photoelectrons.[21] Using the same photoelectron kinetic energy for the Ga $3d$ and As $3d$ spectra also insures that each are indicative of the same part of the near-surface region.

The Ga and As $3d$ core-level spectra were numerically fit in the following manner. First, a smooth background, de-

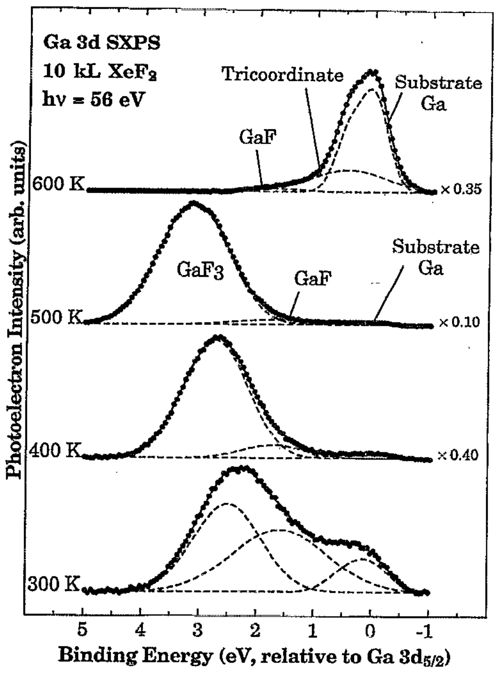

FIG. 2. High-resolution SXPS spectra of the Ga 3*d* core level collected from GaAs(110) surfaces exposed to 10 kL of $XeF_2$ at various temperatures are shown along with numerical fits to the data. The dots show raw data after background subtraction. The dashed lines show the individual components of the fit, while the solid line is the sum of the fit components. Spectra are scaled to equal maximum peak heights, and are labeled with the scaling factor employed and the temperature of the substrate during exposure.

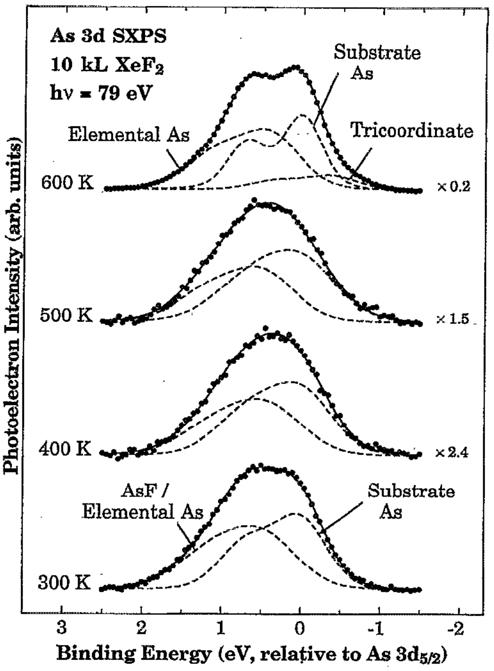

FIG. 3. High-resolution SXPS spectra of the As 3*d* core level collected from GaAs(110) surfaces exposed to 10 kL of $XeF_2$ at various temperatures are shown along with numerical fits to the data. The dots show raw data after background subtraction. The dashed lines show the individual components of the fit, while the solid line is the sum of the fit components. Spectra are scaled to equal maximum peak heights, and are labeled with the scaling factor employed and the temperature of the substrate during exposure.

termined by fitting a third-order polynomial to the data on both sides of the peak, was subtracted from the raw data. Next, all of the core-level spectra were fit, using a least-squares optimization routine, to a sum of Gaussian-broadened Lorentzian spin-orbit split doublets. The fitting procedure was used to find the BE, area, and Gaussian contribution to the width of each core-level component. The Lorentzian full width at half maximum was fixed at 0.12 eV in all of the fits. For the Ga 3*d* core level, the spin-orbit splitting, the branching ratio, and the surface core-level shift relative to the substrate were fixed at 0.45 eV, 0.66, and 0.28 eV, respectively. For the As 3*d* core level, these parameters were fixed at 0.70 eV, 0.65, and $-0.37$ eV, respectively. All these fitting parameters are consistent with previous studies of the GaAs(110) surface.[11,12,21–23]

The chemical composition of the near-surface region is determined from the shifted components in the high-resolution core-level spectra. Once the shifted components are identified, their relative intensities are used to calculate the concentrations of species in the near-surface region. The Ga 3*d* core-level spectra exhibit two chemically shifted components, 1.6 and 2.6 eV higher in BE than Ga in bulk GaAs, which have been identified previously as due to GaF and $GaF_3$, respectively.[6,11,12] As in earlier work, it was not necessary to include an additional component, representative of $GaF_2$, to obtain high quality fits. However, this does not rule out the presence of a small amount of $GaF_2$ on the surface. The position of the chemically shifted component in the As 3*d* spectra, which is 0.5 eV higher in BE than As in bulk GaAs, is consistent with either AsF[11] or adsorbed elemental As.[21,24–26] In addition to the chemically shifted components, there are also shifted core-level components in the clean surface spectra for both Ga and As 3*d* that are due to the surface atoms, which are in a tricoordinate geometry. For a fluorinated surface, there are additional subsurface tricoordinate Ga and As atoms that result from the breaking of substrate bonds during the reaction.[12,27] Since the core-level shifts due to surface and subsurface tricoordinate atoms are nearly equal, they are treated collectively in the fitting procedure.

There are several trends apparent in the Ga 3*d* spectra of Fig. 2. For one, the relative intensity of the $GaF_3$ component increases with $T_s$, whereas the relative intensity of the substrate Ga component decreases slightly, up to 550 K. In addition, the GaF and $GaF_3$ components move toward higher BE with increasing $T_s$, up to 550 K. The increase in BE of the chemically shifted components is attributed to a decrease in electron-hole screening by the substrate electrons as the $GaF_3$ overlayer thickens with increased dosing temperature. A similar shifting towards higher BE with increasing film thickness has been seen for $SiO_2$ films grown on Si.[28] The 600 K spectrum shows no evidence of $GaF_3$ on the surface, but does have small contributions from GaF and from tricoordinate Ga.

In the As 3*d* core-level spectra shown in Fig. 3, the changes due to increased $T_s$ are more subtle. For $T_s$ below 600 K, the intensities of the substrate and high BE As components vary little relative to each other and are both slightly attenuated, relative to the clean surface, with increasing $T_s$.

In the 600 K spectrum, however, in addition to the substrate and high BE components, there is also a tricoordinate As component.

These results indicate that reaction at 600 K generates a GaAs surface that is covered with elemental As. The lack of attenuation in the As and Ga $3d$ photoelectron intensities (see Fig. 1), combined with the absence of a $GaF_3$ component (Fig. 2), indicates that $GaF_3$ does not build up on the surface at 600 K. In fact, the only Ga reaction product on the surface is a residual amount of GaF. However, there is a prominent high BE feature in the As $3d$ spectrum after reaction at 600 K (Fig. 3), which suggests that there is some build up of As reaction products. Since there is essentially no F on the surface following reaction at 600 K, as seen from the near absence of F $2p$ in the valence band spectrum (Fig. 1), it is unlikely that this As $3d$ component has a significant contribution from AsF. Thus, it is attributed to elemental As. Recent high-resolution SXPS data suggests that there are actually two As $3d$ core-level components shifted to higher BE for As adsorbed on GaAs(110).[29] Although the data in the present study are completely consistent with the inclusion of a second shifted As $3d$ component, this does not substantially improve the quality of the fits, since the spectral features are not as well-resolved in the present study as in the work of Ref. 29. Finally, the contributions from tricoordinate Ga and As in the 600 K $3d$ spectra are thought to be due to subsurface defects generated by the reaction, which have been previously observed after the room-temperature reactions of GaAs with $XeF_2$ (Ref. 12) and $Cl_2$.[27]

Once the effects of increasing substrate temperature for a fixed exposure were investigated, a second set of experiments was carried out in which the substrate temperature was held constant and the exposure was varied. SXPS survey spectra are shown in Fig. 4, in order of increasing $XeF_2$ exposure, for reactions at 550 K. This is the highest $T_s$ at which a $GaF_3$ film grows, so that the effects of elevated temperature should be the strongest. As the surface is exposed to $XeF_2$, the F $2p$ valence band feature quickly develops and the weaker and broader F $2s$ core level grows in intensity, indicating that F is incorporated into the near-surface region. The Ga $3d$ core level develops a distinct $GaF_3$ component after as little as a 100 L $XeF_2$ exposure. For higher exposures, this component contributes the majority of the Ga $3d$ core-level intensity. With increasing fluorination, the As $3d$ core level broadens toward higher BE and its intensity is attenuated. The survey spectra change little for exposures above 500 L at the pressures used ($\leqslant 10^{-4}$ Torr), showing that there is a limit to the film thickness. The As $3d$ core level is still visible in the 10 kL survey spectrum, yet no As is expected to be present in the $GaF_3$ film.[12,13] Thus, at its limiting thickness, the overlayer is not thick enough to completely attenuate the As $3d$ photoelectrons originating from the substrate and interface.

However, a thick film was grown by exposing the GaAs wafer to the vapor pressure of $XeF_2$ (~4 Torr) for 1000 s. An SXPS survey spectrum from this thick film is also shown in Fig. 4. The thickness of the film could not be determined, but it was large enough that there were visible changes in the appearance of the sample surface as well as problems due to sample charging during measurement. There is no contribution from As $3d$ visible in the survey spectrum taken from the thick film, confirming the fact that As is completely removed from the near-surface region. The lack of detectable As signal in the survey spectrum indicates that the film is at least 40 Å thick. That is, for the photon energies used, the As $3d$ photoelectron intensity collected from a GaAs surface covered with a 40-Å-thick $GaF_3$ film would be roughly 0.1% of that originating from a clean surface, making it comparable to the noise level.

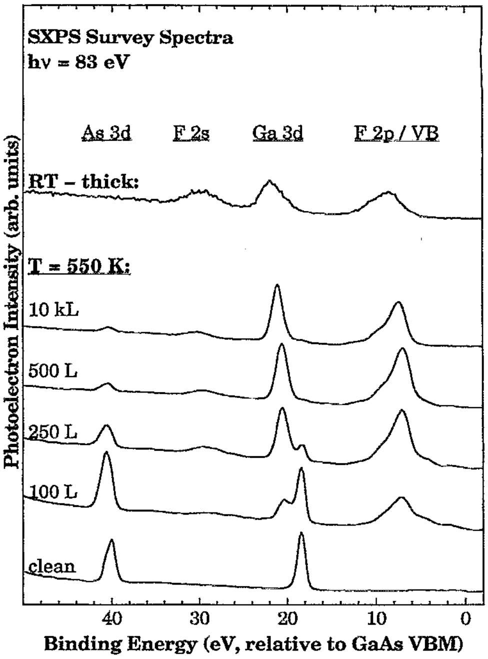

FIG. 4. SXPS survey spectra collected from GaAs(110) surfaces exposed at 550 K to $XeF_2$. Spectra are scaled to the same maximum peak height, and are labeled by the $XeF_2$ exposure. A survey spectrum from a thick $GaF_3$ film grown at room temperature is shown for comparison.

High-resolution Ga $3d$ and As $3d$ core-level spectra are shown in Figs. 5 and 6, together with numerical fits to the data, for samples exposed at 550 K. The clean-surface spectra each contain substrate and tricoordinate components. With increasing fluorination, the tricoordinate components vanish, the As $3d$ spectrum develops a high BE component, and the Ga $3d$ spectrum develops both monofluoride and trifluoride components. Further fluorination causes the intensity of the $GaF_3$ component to increase, whereas the intensities of the other Ga $3d$ and As $3d$ components are attenuated. This behavior is similar to that reported in previous room-temperature investigations, in which a $GaF_3$ film grows, As is removed from the near-surface region, and the underlying substrate is covered by the film.[11,12]

## IV. FILM AND INTERFACE THICKNESS CALCULATIONS

In order to calculate the film and interface thicknesses from the relative intensities of the core-level components in the SXPS spectra, certain simplifying assumptions are made. The near-surface region is considered to be composed of a

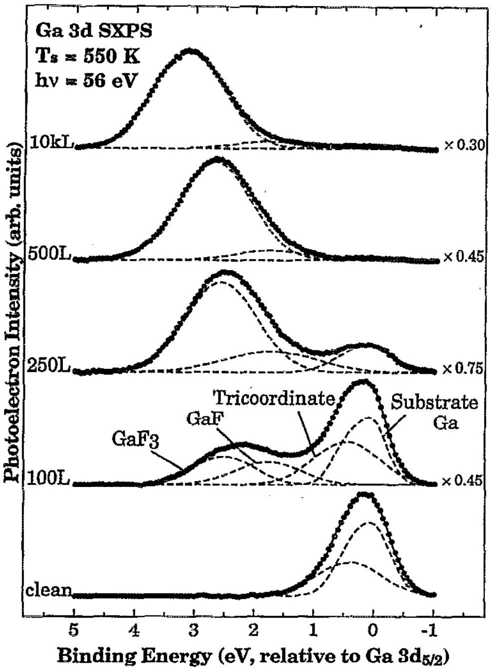

FIG. 5. High-resolution SXPS spectra of the Ga $3d$ core level collected from a clean GaAs(110) surface and from surfaces exposed at 550 K to $XeF_2$ are shown along with numerical fits to the data. The dots show raw data after background subtraction. The dashed lines show the individual components of the fit, while the solid line is the sum of the fit components. Spectra are scaled to equal maximum peak heights, and are labeled with the scaling factor employed and the temperature of the substrate during exposure.

uniform film of $GaF_3$ with an interface to the substrate consisting of a homogeneous mixture of GaF, elemental As, and/or AsF. This model for the distribution of species is based on earlier sputter/Auger depth profiles of $GaF_3$ films on GaAs,[13] a TEM measurement,[5] and two previously proposed models for $GaF_3$/GaAs.[3,12] Although the present data cannot be used to independently determine the distribution of chemical species in the near-surface region, it is consistent with the conclusions of the earlier work. Due to the possibility of F-induced changes in stoichiometry, the relative concentrations of Ga and As in the interface and in the region of the substrate visible to SXPS are not assumed to be fixed in this analysis, but rather are determined from the analysis. The total density of Ga plus As in each of these regions is, however, set to the value for crystalline GaAs and the density of Ga in the $GaF_3$ film is then taken to be half of that value, which is correct to within ~5%. The Ga $3d$ and As $3d$ photoelectrons are assumed to be attenuated exponentially with increasing depth into the sample, with an attenuation length of $\lambda = 5.5$ Å.[21] The atomic photoionization cross sections of the Ga $3d$ ($\sigma_{\rm Ga}$) and As $3d$ ($\sigma_{\rm As}$) core levels calculated by Yeh and Lindau[30] are used so that photoelectron intensities from Ga and As can be compared, with the assumption that these cross sections are unchanged by fluorination.

Under these assumptions, the relative intensities of the core-level components are converted into more meaningful quantities, namely the thicknesses of the film ($D$) and interface region ($d$) and the interface As to Ga ratio ($r$). This is

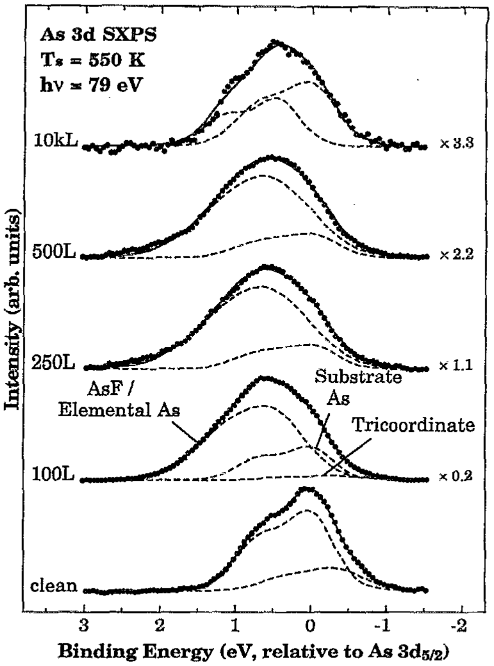

FIG. 6. High-resolution SXPS spectra of the As $3d$ core level collected from a clean GaAs(110) surface and from surfaces exposed at 550 K to $XeF_2$ are shown along with numerical fits to the data. The dots show raw data after background subtraction. The dashed lines show the individual components of the fit, while the solid line is the sum of the fit components. Spectra are scaled to equal maximum peak heights, and are labeled with the scaling factor employed and the temperature of the substrate during exposure.

done to remove any effects arising from the attenuation of the interface signal by the $GaF_3$ overlayer, which makes any changes in the chemical concentrations at the interface more apparent. This analysis leads to the following equations, which relate the core-level component intensities to $r$, $d$, and $D$:

$$D = \lambda \ln\left(1 + \frac{2R_4}{1 + R_3 + (\sigma_{\rm Ga}/\sigma_{\rm As})(R_1 + R_2 R_3)}\right), \tag{1}$$

$$d = \lambda \ln\left(1 + R_3 \frac{\sigma_{\rm As} + \sigma_{\rm Ga} R_2}{\sigma_{\rm As} + \sigma_{\rm Ga} R_1}\right), \tag{2}$$

$$r = R_2 \frac{\sigma_{\rm Ga}}{\sigma_{\rm As}}, \tag{3}$$

where $R_1$ is the substrate As $3d$ to substrate Ga $3d$ intensity ratio, $R_2$ is the interface As $3d$ to interface Ga $3d$ intensity ratio, $R_3$ is the interface Ga $3d$ to substrate Ga $3d$ intensity ratio, and $R_4$ is the $GaF_3$ $3d$ to substrate Ga $3d$ intensity ratio, all derived from fitting the high-resolution spectra.

Since it is likely that the actual physical system is not as well-ordered as is assumed by this model, the numbers determined in this manner do not necessarily provide accurate film thicknesses. For example, the Ga and As products in the interface may be layered or in some other way not homogeneously mixed, and/or the film and interface regions may not be uniformly thick. However, although there are inherent uncertainties in the numbers generated using the above assumptions, they are still adequate for a comparison of trends in spectra collected from different samples.

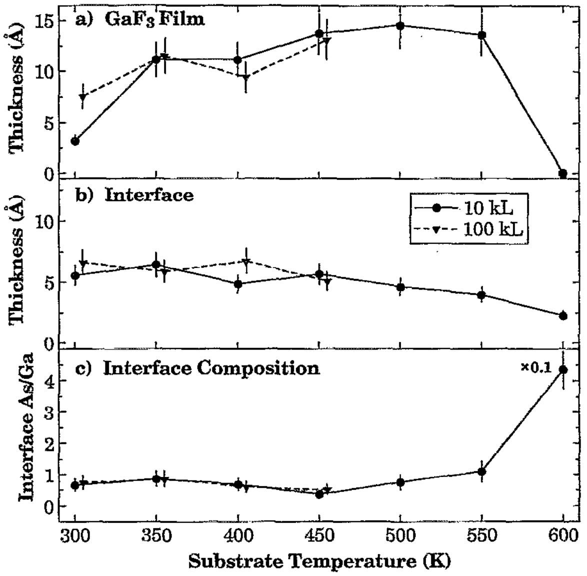

FIG. 7. Calculated $GaF_3$ film thickness, interface thickness, and interface As/Ga ratio are shown as a function of substrate temperature for GaAs(110) surfaces exposed to 10 and 100 kL of $XeF_2$.

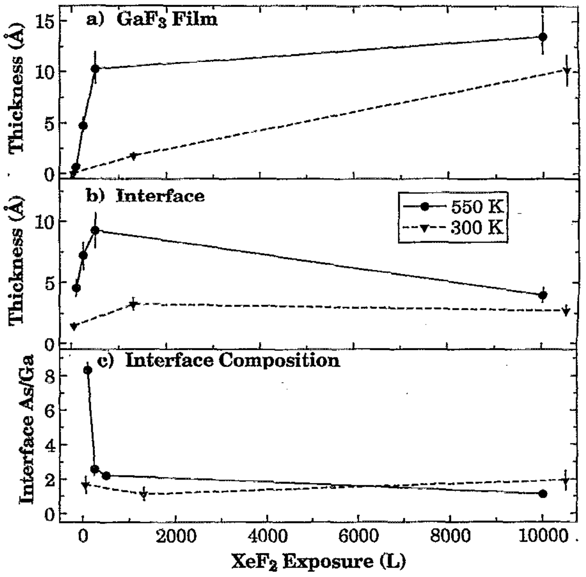

FIG. 8. Calculated $GaF_3$ film thickness, interface thickness, and interface As/Ga ratio are shown as a function of $XeF_2$ exposure for GaAs(110) surfaces exposed at 300 and 550 K.

The calculated $GaF_3$ film thickness, interface thickness, and interface composition are shown as a function of temperature in Fig. 7 for surfaces exposed to 10 and 100 kL of $XeF_2$. As $T_s$ increases from 300 to 550 K, the $GaF_3$ film thickness increases by 5 to 10 Å and the interface thickness decreases slightly, whereas the interface composition remains fairly constant. After exposure at 600 K, however, there is a complete absence of $GaF_3$, the interface thickness is only half of its room-temperature value, and the interface is composed almost entirely of As. Note that the film and interface thicknesses remain essentially unchanged following a tenfold increase in exposure, i.e., from 10 to 100 kL [Fig. 7(a)], which indicates that the film has reached a limiting thickness. Further, note that the value of the final thickness is nearly independent of temperature for $T_s \leq 550$ K.

Figure 8 shows the $GaF_3$ film thickness, interface thickness, and interface composition as a function of exposure for films grown at 550 K. Some data for films grown at 300 K are also shown for comparison. It appears that the films grow more rapidly at elevated temperatures. Initially, the interface thickens at a greater rate and to a greater extent at the higher temperature. In fact, the 550 K interface appears to overshoot its final thickness by a factor of 2 before leveling out at ~5 Å. The interface grown at 550 K begins As rich and becomes less so with increased fluorination. Since the clean GaAs sample was slightly Ga rich, however, it is the initial fluorination that causes the surface to become As rich. This initially high As content can be explained either by the selective removal of Ga from the surface, as suggested in Ref. 27, or by fluorine-induced As surface segregation, similar to the chlorine-induced surface segregation of As proposed in earlier studies of $Cl_2$/GaAs reactions.[31–35]

## V. DISCUSSION

The following model for the mechanism of $GaF_3$ film growth via exposure of GaAs to $XeF_2$ is proposed, based on analysis of the data presented here and by Varekamp *et al.*[12] First, $XeF_2$ molecules dissociate on the surface, liberating F atoms, which react rapidly with Ga forming first monofluorides and then, at a lesser rate, difluorides that quickly react to form the more stable trifluorides. The relative rates of Ga fluoride formation are inferred from the fact that little or no difluoride is evident in any of the SXPS spectra. In addition to Ga fluoride formation, the reaction also leads to the removal of As from the surface, either as elemental As or as an As fluoride species. Ga–As bonds are broken throughout the reaction, generating tricoordinate Ga and As atoms at the interface between the fluoride layer and the substrate.

The initial reaction is rapid because atomic F is highly reactive and there are many bonding sites available on the clean surface. Then, as surface sites become tied up, the F adsorption rate decreases and the reaction slows. Passivation of all the surface sites does not completely halt the reaction, however, since substrate bonds are broken as a result of the reaction, which continually generates new sites for adsorption. This initial F adsorption stage is temperature dependent, with the initial rate being faster at higher substrate temperatures.

The initial dissociation rate of $XeF_2$ on GaAs is expected to exhibit a temperature dependence similar to that for its reaction with Si, which shows a minimum in the reaction rate between 360 and 450 K.[36] For Si, below 360 K, the reduction of the reaction rate with increasing temperature is attributed to a decreased surface residence time prior to dissociation, since the $XeF_2$ molecules presumably physisorb into a precursor state due to an image charge interaction between the molecules and the surface. Above 450 K, however, the reaction rate of $XeF_2$ with Si increases with temperature as a consequence of the kinetics of the chemical reaction. For the present data, an increase in the initial reaction rate with $T_s$ is observed in going from 300 to 550 K [see Fig. 8(a)]. However, there is not enough information to ascertain whether or not the rate of $XeF_2$ dissociation on GaAs reaches a minimum at some temperature below 300 K.

After enough $GaF_3$ builds up to cover the surface, the chemical reaction between F and GaAs must take place below the surface at the film–substrate interface. In this way, the reaction continues, pushing the interface down into the substrate, until the film reaches its limiting thickness of 10 to 15 Å. Throughout this stage of the reaction, diffusion of F from the surface to the interface, as well as diffusion of As from the interface to the surface, is occurring. Although it might be thought that the film would act as a barrier to diffusion, this does not appear to be the case. A diffusion limited reaction would show a strong temperature dependence in the limiting film thickness, which is not observed. Therefore, there is some other reason for the observed thickness limit.

One possible explanation is the following. Due to its large size, a $XeF_2$ molecule cannot easily diffuse through the $GaF_3$ film in order to react at the interface. Thus, to contribute F to the reaction, $XeF_2$ must dissociate on the surface. As the GaAs surface becomes covered with $GaF_3$ there will be a reduction in the image charge interaction between $XeF_2$ molecules and the surface, resulting in a shorter residence time for $XeF_2$ on the surface and thus a decreased probability for dissociation. In addition, $GaF_3$ films grown in this manner take on the electronic structure of bulk $GaF_3$ once they reach a thickness of $\sim$10 Å.[12] Since $GaF_3$ is an insulator, there are fewer free electrons available to aid in the dissociation of $XeF_2$ at the surface, which results in the reduced production of F atoms for films thicker than $\sim$10 Å, analogous to the observed lack of $XeF_2$ dissociation on $SiO_2$ thin films.[37] These effects could combine to severely reduce the film growth rate once the surface is covered with $GaF_3$. In fact, film growth would cease if $XeF_2$ were completely unable to dissociate on $GaF_3$ or to diffuse through the film to the interface.

The upper limit to the film thickness can be overcome by increasing the pressure, and thus the exposure, by several orders of magnitude. This upper limit is most apparent in Fig. 7(a), in which it is shown that, for $T_s$ ranging from 350 to 550 K, an order of magnitude increase in exposure to $XeF_2$ does not measurably increase the $GaF_3$ thickness. Yet, a thicker film can be grown if the pressure is increased several orders of magnitude, as shown in Fig. 4. Unfortunately, it is not possible to determine from the present data whether film growth actually ceases at low pressures or if it just slows considerably, i.e., whether growth is ultimately pressure or exposure limited. It is likely that at higher pressures a new mechanism is responsible for film growth, and further study is thus needed before film growth at higher pressures can be adequately explained.

More insight into the F/GaAs reaction can be gained by a comparison to $Cl_2$/GaAs, which has been studied to a greater extent. For instance, there is evidence of a slight preference for the formation of Ga–Cl bonds over As–Cl bonds.[27,38] This preference can be explained by the difference in their bond strengths, as the Ga–Cl bond (5.0 eV) is slightly stronger than the As–Cl bond (4.6 eV).[39] Another important effect is that there are two competing pathways for the removal of As, as observed in $Cl_2$/GaAs molecular beam scattering experiments.[40–42] Arsenic chlorides are formed at low temperatures, with $AsCl_3$ being the major As-containing gaseous reaction product. At high temperatures, however, $As_2$ and $As_4$ are produced. The transition between the low- and high-temperature behavior occurs somewhere between 400 and 550 K. This transition has been predicted by thermodynamic arguments,[43] and may be due to the instability of As chlorides at elevated temperatures. Since Ga–Cl bonds are stronger than As–Cl bonds, Ga chlorides are still stable at temperatures at which As chlorides begin to decompose, resulting in the apparent reduction of As chlorides by Ga. The reduction of As chlorides[44] (and also of As fluorides[3]) by Ga at elevated temperatures has been proposed previously. It therefore appears that the disparity in Ga–Cl and As–Cl bond strengths, in large part, determines the outcome of the $Cl_2$/GaAs reaction.

It is likely that the F/GaAs reaction behaves in a similar fashion. In fact, the difference between the Ga–F (6.0 eV) and As–F (4.3 eV) bond strengths is over four times greater than the difference between Ga–Cl and As–Cl bonds,[39] which suggests an even stronger preference for Ga bonding. Also, since the As–F bond is weaker than the As–Cl bond, As fluorides should become unstable at a lower temperature than As chlorides, and thus the transition from As fluoride to elemental As formation should occur at a lower $T_s$, possibly even below room temperature. It is therefore likely that the major As-containing gaseous reaction product evolved in the temperature range studied in the present investigation is elemental As, and not $AsF_x$. These considerations are by no means conclusive, however. A molecular beam scattering experiment is needed to directly measure the reaction product distribution as a function of $T_s$.

Although it is uncertain whether the major As surface reaction product is AsF or elemental As, for $T_s$ below 600 K, there are still some conclusions that can be made about the role of As in the reaction. First, the high BE component in the As $3d$ spectrum for reaction at 600 K is due to elemental As, and not to AsF, and it is likely that this result extends to lower temperatures. In fact, the formation of free As in the reaction at lower temperatures would help to explain how As is removed from the interface during the reaction, since an As atom would diffuse through the $GaF_3$ film more readily than a larger As fluoride molecule. Second, it appears that only a limited amount of As is stable at the interface. From the interface thicknesses and As/Ga ratios given in Figs. 7(b) and 7(c), it is seen that there is $\sim$2 Å of As present at the interface, independent of $T_s$. This corresponds to $\sim$1 monolayer of As, which is consistent with the measured saturation coverage of elemental As on GaAs(110).[45]

This film growth mechanism only applies for temperatures up to 550 K. For temperatures above $\sim$550 K, the data indicate that $XeF_2$ etches GaAs. Etching proceeds via the reaction of Ga with F to form $GaF_3$, which immediately desorbs since it is unstable on the surface at temperatures above $\sim$573 K.[16] The As left behind then builds up to a thickness of about 1 monolayer. Any additional elemental As desorbs, most likely as $As_2$ and/or $As_4$. In this way, both Ga and As are removed in the 600 K reaction of GaAs with F.

## VI. SUMMARY

$GaF_3$ films were grown on GaAs(110) wafers via exposure to $XeF_2$ and examined with SXPS to determine how the substrate temperature during film growth affects the $GaF_3$–GaAs interface. For temperatures between 300 and 550 K, a $GaF_3$ film forms on top of the GaAs substrate. Between the substrate and film is an interface region consisting of GaF, elemental As, and possibly some AsF. Raising the substrate temperature accelerates the initial F uptake rate, while increasing exposure at these temperatures thickens the $GaF_3$ film up to a limiting value, which can be overcome by greatly increasing the pressure. There is little change in the thickness or composition of the interface as substrate temperature is increased. All of this is explained by a reaction mechanism in which F atoms liberated at the surface react at the film–substrate interface, generating $GaF_3$ while removing As from the near-surface region, thus pushing the interface down into the substrate as the film grows. Above 550 K, F etches GaAs, leaving a surface covered by $\sim 1$ monolayer of elemental As.

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